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Bio-based polyurethane films using white dextrins

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ABSTRACT: Several new eco-friendly materials have the potential to replace conventional petroleum-derived materials and monomers. Among them are natural polysaccharides. The use of polysaccharides in polyurethane (PU) synthesis has not yet been studied extensively, even though as multihydroxyl compounds, they can easily serve as crosslinkers in PU synthesis. One naturally occurring (hyper-) branched polymer is amylopectin, a component of starch. In this work, we report the PU synthesis and film-forming capacity using the asymmetric cyclic aliphatic diisocyanate—isophorone diisocyanate (IPDI) with acetylated and pristine partially hydrolyzed amylopectin/white dextrin (AVEDEX W80) as a crosslinker. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 47454.

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INTRODUCTION

Polyurethanes (PUs) are high-performance polymers that show excellent properties, such as chemical, abrasion, and scratch resistance, as well as flexibility and toughness. Changes in the nature of the polyols, di-/multi-isocyanates, and catalysts or other additives allow the synthesis of different end polymers. Industries operating in the PU sector are strongly dependent on fossil-based polyols and polyisocyanates. In recent years, the preparation of PUs from renewable sources such as vegetable oil-based materials,[1] lignin,[2] limonene,[3] and even coffee grounds[4] has been receiving increasing attention because of the economic and environmental concerns.[5]

The use of carbohydrates in PU synthesis has not yet been studied extensively, even though, as multihydroxyl compounds, they can easily serve as crosslinkers in PU synthesis. Furthermore, they can impart mechanical strength, biodegradability, and biocompatibility to the produced PUs. Carbohydrates are reported to be embedded in PU networks using them as composites/fillers and by covalent linkage with isocyanate to form crosslinked networks.[6] Solanki *et al.*, for instance, synthesized castor oil-based PUs crosslinked with starch and reported excellent mechanical properties of the produced materials.[7] Carbohydrates, such as cellulose[8–12] or starch[13] nanocrystals, have been used as useful fillers in PUs.

Highly branched polysaccharides hold a high amount of functional groups per molecule,[14–16] which is especially attractive for industrial purposes,[17] offering high functionality,[18,19] broad variety of functional groups, high solubility, and unique rheological behavior.[20–27] Therefore, branched polysaccharides seem to be an appropriate choice for developing a performance coating material based on renewable biomass-derived hyper-branched polysaccharides.

In our recent work, we reported the esterification (acetylation, propionation, and esterification with longer fatty acids) of white dextrines (degraded starches) and "waxy potato" starch containing more than 95% amylopectin.[28] A very important feature of this reaction is the fact that the esterified material does not undergo a color change due to the mild reaction conditions. This can be very important for various industrial applications, such as coatings, films, and so on.

In this work, we report the PU synthesis and film-forming capacity using the asymmetric cyclic aliphatic diisocyanate—isophorone diisocyanate (IPDI) and acetylated and pristine partially hydrolyzed amylopectin/white dextrin (AVEDEX W80) as a crosslinker.

MATERIALS AND METHODS

Already degraded amylopectin/white dextrin (AVEDEX W80) was obtained from AVEBE (Veendam, The Netherlands) and used without further purification. Iodine was provided by Boom and purified by sublimation twice. Acetic anhydride (Ac_2O) (≥99.0%) was provided by Fluka, sodium thiosulfate (NaS_2O_3) (≥98.0%) and dimethyl sulfoxide (DMSO) (99%) were provided by Sigma-Aldrich, and ethanol (≥99%) was purchased from Merck KGaA and used without further purification. IPDI was provided by Merck and purified by distillation.

Proton nuclear magnetic resonance spectra were recorded on a Varian VXR spectrometer (400 MHz). The reported chemical shifts were referenced to the resonances of the residual solvent or tetramethylsilane (TMS). Attenuated total reflection-Fourier transform infrared (ATR-FTIR) measurements were characterized by a Bruker IFS88 FT-IR spectrometer. For each sample, 128 scans were performed.

Synthesis of Polyols

In a round-bottom flask equipped with a magnetic stirring bar, 2 g (11.1 mmol) AVEDEX W80 was dissolved in 1.57 mL (16.6 mmol) acetic anhydride. After adding 120 mg iodine, the mixture was heated at 100°C for 10 min. After cooling to room temperature, the mixture was treated with a saturated solution of sodium thiosulfate, with the mixture's change in color from purple-brown to colorless indicating the transformation of iodine to iodide. The mixture was poured in 100 mL of ethanol and stirred for 30 min. After filtration and washing with water, the final product was dried in vacuo. This reaction can be modified in several ways, including the Ac_2O:AGU (anhydroglucose unit) ratio, reaction time and temperature, the acylating agent (acetic/propionic anhydride), amount of catalyst, precipitating agent, and washing agent. The influence of reaction conditions on the degree of substitution (DS) and methods for obtaining the desired DS were recently reported by us.

Crosslinking of Acylated Polyols with Diisocyanates

About 0.1 g of acetylated polyol or pristine AVEDEX W80 was dissolved in 2 mL of solvent (DMSO or 1-methylimidazole). A 1.05-fold excess of a diisocyanate (1.05-fold excess of —NCO groups to —OH groups) was added, and the mixture was stirred for 2–3 min until a homogenous mixture was obtained. This mixture was then poured onto a Petri dish, which was placed on a heating block at a defined temperature, covered with filter paper, and enclosed together with the heating block to provide a solvent atmosphere. After a defined period of time, the Petri dish was removed from the heating block. Films were analyzed via FTIR. This procedure can be scaled up several folds to obtain larger films.

RESULTS AND DISCUSSION

Using a iodine-catalyzed esterification reaction, it is possible to esterify short (AVEDEX W80) and long (ELIANE) carbohydrates up to a DS of 3. The reaction using acetic anhydride as an acylating agent proceeds the fastest as compared to those using longer fatty acids. In these reactions, the desired DS can be achieved using the right ratio of catalyst to anhydroglucose units.[28]

To verify the usability of these modified carbohydrates as polyol components in coatings, their crosslinking with isocyanates is studied. In general, there are two established methods: the first method is a direct crosslink of the polyol with a slight excess of diisocyanates followed by chain extension with diols or diamines; the second method, the so-called two-step method, includes the end-capping of the acylated polyol with a huge excess of diisocyanates and removal of residual diisocyanate by distillation. The second step of this method consists of chain extension of the end-capped polyol with diols, diamines, diacids, or urethane building blocks.

In this study, we focus on the first method for crosslinking of the obtained modified and pristine carbohydrate-based polyols. IPDI was used due to the current tendency in industry to substitute aromatic diisocyanates with aliphatic diisocyanates.[29–31] In addition, toluene diisocyanate (TDI)- and methylene diphenyl diisocyanate (MDI)-based PUs are less thermally stable, decomposing at lower temperatures than aliphatic isocyanate-based foams.[32] According to prior research, catalysts are necessary for successful PU formation with IPDI due to the low reactivity of isocyanate groups toward hydroxyl groups.[31] In this research, however, we found that at small scales, no catalyst is necessary. In a follow-up study, we will follow the kinetics of this reaction in more detail.

To study the feasibility of PU synthesis of modified and pristine AVEDEX W80 with IPDI, the reaction conditions were varied in several ways (e.g. casting time and temperature, amount of solvent, and excess of diisocyanate) and the results were compared in solvent casting experiments to form films.

DMSO and 1-methylimidazole were tested as reaction and film casting solvents, as they are good solvents for the modified carbohydrates. From Figure 1, it becomes obvious that DMSO delivered by far better results than 1-methylimidazole. Obviously, the higher dipole moment of DMSO results in a better suspension of the resulting PU longer leading to a better film formation. Additional initial experiments revealed that low-DS carbohydrates form uniform films whereas high-DS samples resulted in a brittle and fractured film. Apparently, it is important that most or all OH groups of the branched polysaccharides are fully available for the reaction. Good film formation within 6–8 h was observed, while casting times of <6 h resulted in wet samples and casting times of 8–10 h resulted in brittle samples; see Figure 2(a). In the FTIR spectra of PU films after different casting times, it becomes obvious that the urethane formation continues even after 8 h

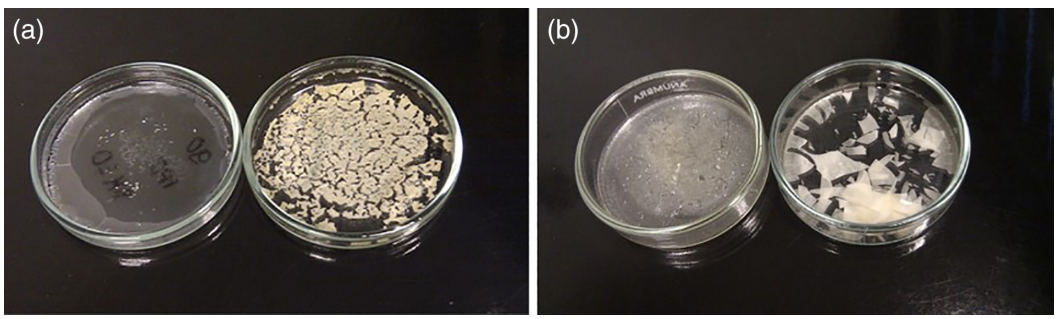

Figure 1. (a) Solvent cast film of acetylated AVEDEX W80 (DS = 2.5) from DMSO (left) and 1-methylimidazole (right) and (b) solvent cast film of acetylated AVEDEX W80 with low DS (DS = 0.4) (left) and high DS (DS = 2.8) (right). [Color figure can be viewed at wileyonlinelibrary.com]

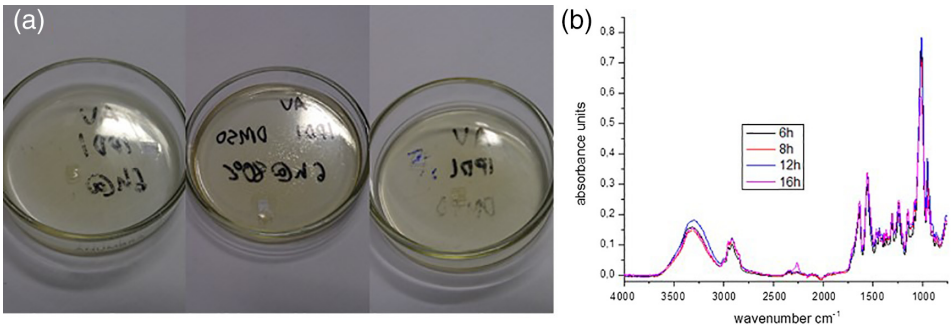

Figure 2. (a) Pictures of AVEDEX W80-IPDI PU films with a casting time of 6, 8, and 12 h, respectively, and (b) FTIR spectra of AVEDEX W80-IPDI PU films with different casting times. [Color figure can be viewed at wileyonlinelibrary.com]

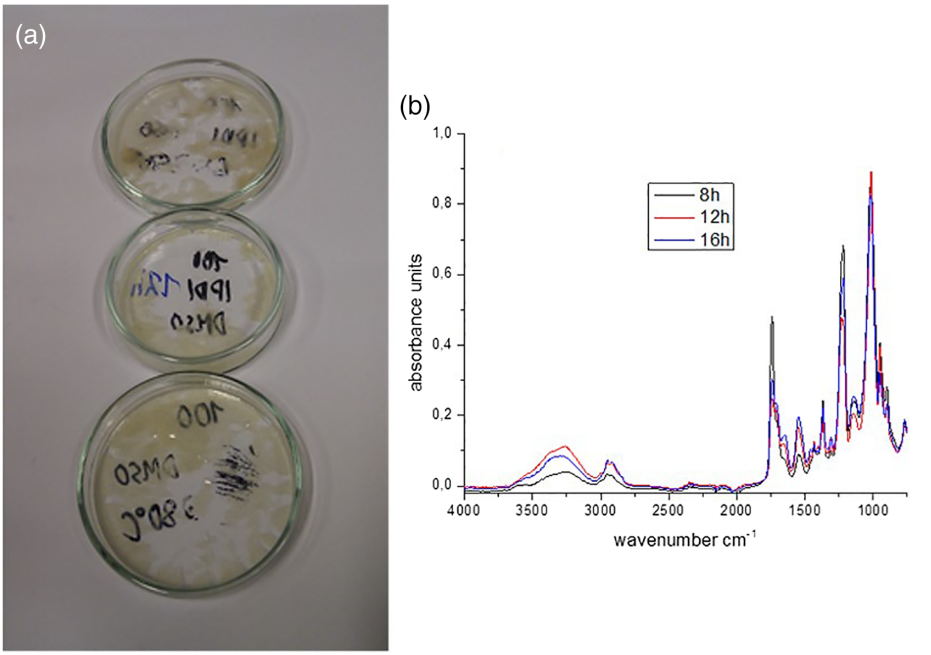

Figure 3. (a) Pictures of acetylated AVEDEX W80 (DS 2.8)-IPDI PU films with a casting time of 6, 8, and 12 h, respectively, and (b) FTIR spectra of acetylated AVEDEX W80 (DS 2.8)- IPDI PU films with different casting times. [Color figure can be viewed at wileyonlinelibrary.com]

resulting in the brittleness of the films due to excessive crosslinking. The peaks of the amide I and amide II bands from the newly formed polyurethane linkages are visible at 1550 cm^{-1} and 1650 cm^{-1}, respectively.

Figure 3(a) clearly shows that PU films produced from a high-DS carbohydrate polyol are very brittle, no matter the casting time and temperature. The FTIR spectra in Figure 3(b) confirm a successful urethane formation, whereas the ester peak at around 1750 cm^{-1} is still visible. In this case, the brittleness cannot be a result of excessive crosslinking as most OH groups of the branched polysaccharide are esterified.

CONCLUSIONS

PU films can be easily synthesized using the asymmetric cyclic aliphatic diisocyanate—IPDI and acetylated and pristine partially hydrolyzed amylopectin/white dextrin (AVEDEX W80) as a crosslinker. Partially acetylated AVEDEX80 results in brittle films, whereas unmodified white dextrin is able to form stable films in which all isocyanate functions are converted. The best results were obtained using unmodified AVEDEX W80 as polyol, DMSO as solvent, a casting time between 6 and 8 h, and a casting temperature of 80 °C.

Further research into the type of esterification, type of carbohydrate, and di- or multi-isocyante will be conducted in the near future.

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